

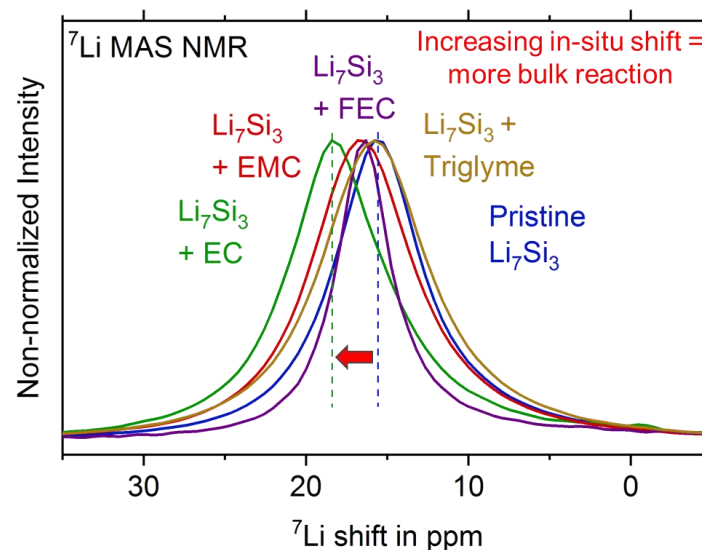
# ACTIVE PARTICLE STUDIES

## BARIS KEY

U.S. DEPARTMENT OF ENERGY  
 VEHICLE TECHNOLOGIES OFFICE  
 2018 ANNUAL MERIT REVIEW

## Silicon Deep Dive

in-situ NMR



Project ID BAT351

# OVERVIEW

## Timeline

- Start: October 1, 2015
  - Reset: October 1, 2017
- End: September 30, 2020
- Percent Complete: 55%

## Budget

- Total project funding:
  - FY18 - \$3600K
- Presentations: BAT349, BAT350, BAT351, BAT352, and BAT353

## Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost, Performance, and Safety

## Partners

- Sandia National Laboratories
- Pacific Northwest National Laboratory
- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Argonne National Laboratory

# RELEVANCE

- Objectives: Stabilize the SEI - Stabilize the electrode
- Overall focus on insights into and advancement of silicon-based materials, electrodes, and cells.
- Advancements verified on life and performance of full cells using standardized testing protocols.

## Program Directly Addresses Cost and Performance Barriers and Quantifies Safety

- Elemental silicon can theoretically store  $>3500$  mAh/g.
- Battery Performance and Cost (BatPaC) Model indicates a silicon based anode coupled with a high capacity cathode lithium-ion technology presents a pathway to less than  $\$125/\text{kWh}_{\text{use}}$
- BatPaC also used to relate pack level benefits to program goals.
- Benefits reach diminishing returns after **1000 mAh/cm<sup>3</sup>** (electrode basis) for both cost and energy density.
- Silicon with  $<75$  wt% graphite can achieve target.

# MILESTONES AND ACTIVITIES

- **The program has more than twenty milestones related to the broad range of integrated activities listed below.**
- **Generally, milestones are either completed or on schedule.**
- Extensive electrochemical and analytical diagnostic studies.
- Facilities supporting program through a wide range of studies.
  - Battery Abuse Testing Laboratory (BATLab); Battery Manufacturing Facility (BMF); Cell Analysis, Modeling, and Prototyping (CAMP) Facility; Materials Engineering Research Facility (MERF); Post-Test Facility (PTF)
- Development and testing of coatings and additives designed to modify and stabilize the interface.
- Develop and analyze polymer binders designed to accommodate volume changes, increase conductivity, and improve adherence.
- Active material development.
  - Explore lithium inventory strategies.
  - Study alternative high-energy metals.

For reviewers, a detailed list of the milestones and progress is supplied in the reviewers only slides.

# APPROACH

## Use local structure probes (NMR, FTIR, Raman) along with diffraction to study commercial silicon powders and model compound reactions

- Probe amorphous and crystalline components of commercial silicon powders and their structure activity relationships
  - Effects of processing
  - Heat treatments pre-electrochemistry
  - Correlating changes in surface terminations
- Probe major reactions that may cause coulombic inefficiencies and self-discharge, study the best representative model compounds of Li-Si system:
  - **$\text{Li}_7\text{Si}_3$  ← current focus**
  - $\text{Li}_{13}\text{Si}_4 + \text{Li}_{15+x}\text{Si}_4$ : future work
  - Study the reactivity of lithium silicides,  $\text{Li}_x\text{Si}_y$ , with different electrolyte components and binders to understand the reaction mechanism that Si-based anodes may undergo.

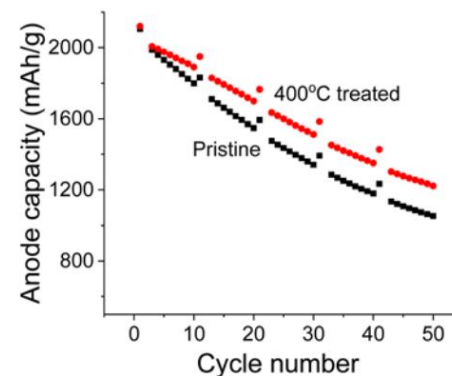
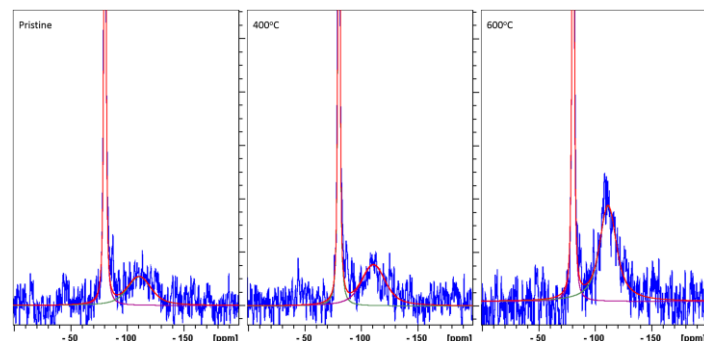
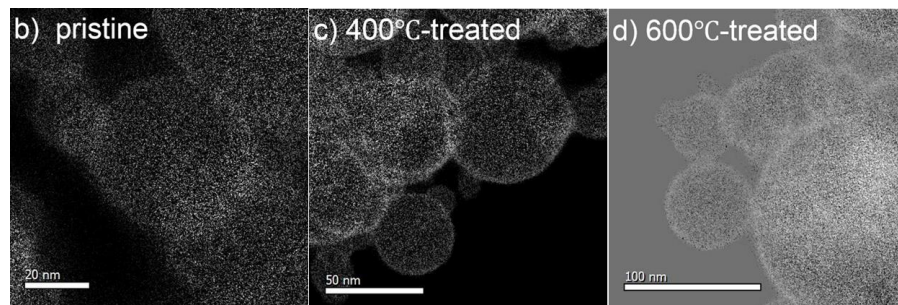
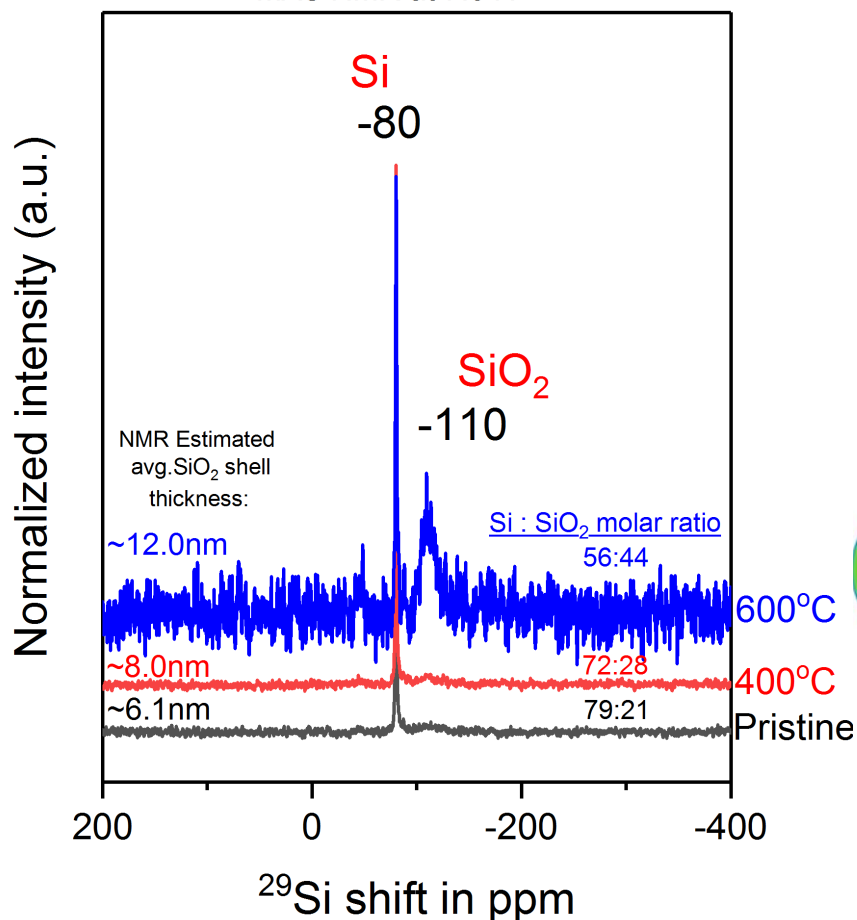
# PROBING BULK AND SURFACE CHEMISTRY OF SILICON

ACS Applied Materials & Interfaces, 9 (38), 32727-32736

## Quantification of amorphous SiO<sub>2</sub> content with NMR

See BAT352

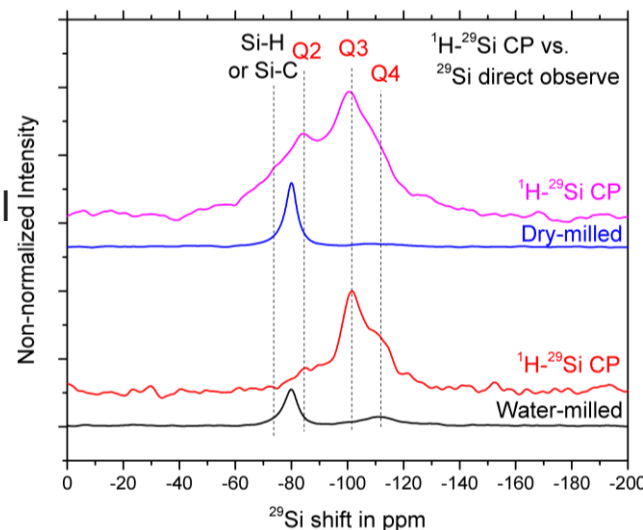
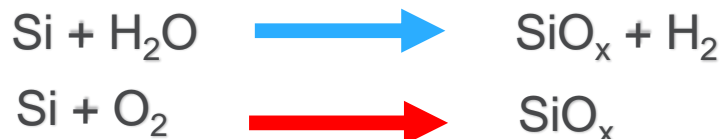
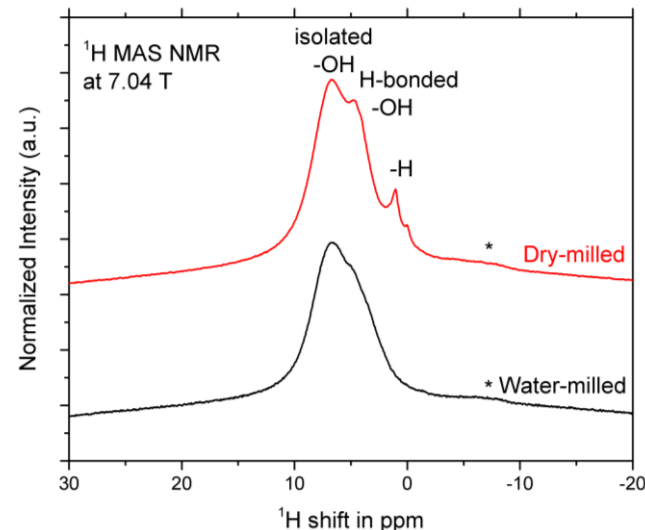
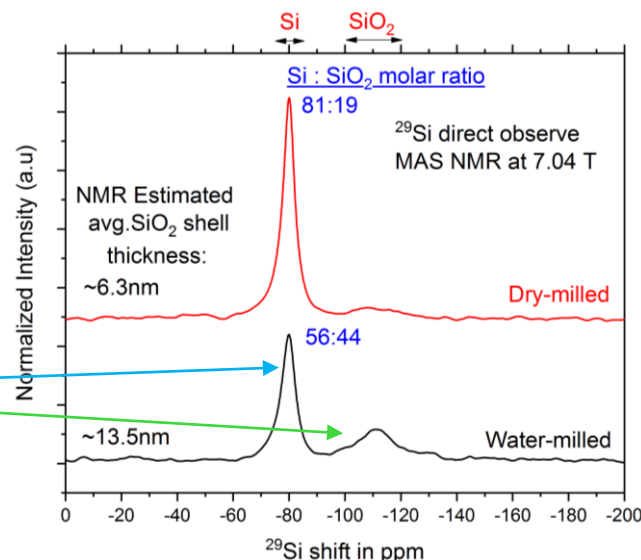
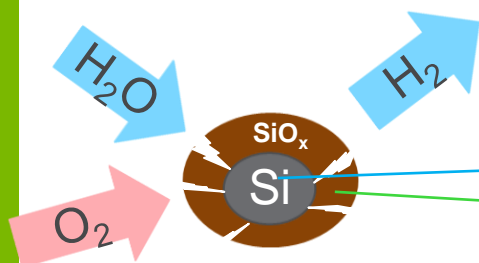
<sup>29</sup>Si direct observe  
MAS NMR at 7.04T



# PROBING BULK AND SURFACE CHEMISTRY OF SILICON

## Bulk and surface structure effects of processing conditions

See BAT345 and 349



- Water processed commercial Si powder amorphous SiO<sub>2</sub> shell thickness increase of 7.5nm captured directly via <sup>29</sup>Si NMR
- The <sup>1</sup>H and <sup>1</sup>H-<sup>29</sup>Si cross polarization MAS NMR displays the transition of Si-H, geminal (Q<sub>2</sub>), and siloxane (Q<sub>4</sub>) sites to silanol sites (Q<sub>3</sub>). This likely occurs when water oxidizes the Si-H sites to Q<sub>3</sub> sites

Hays *et al.*, submitted to JPC, 2018

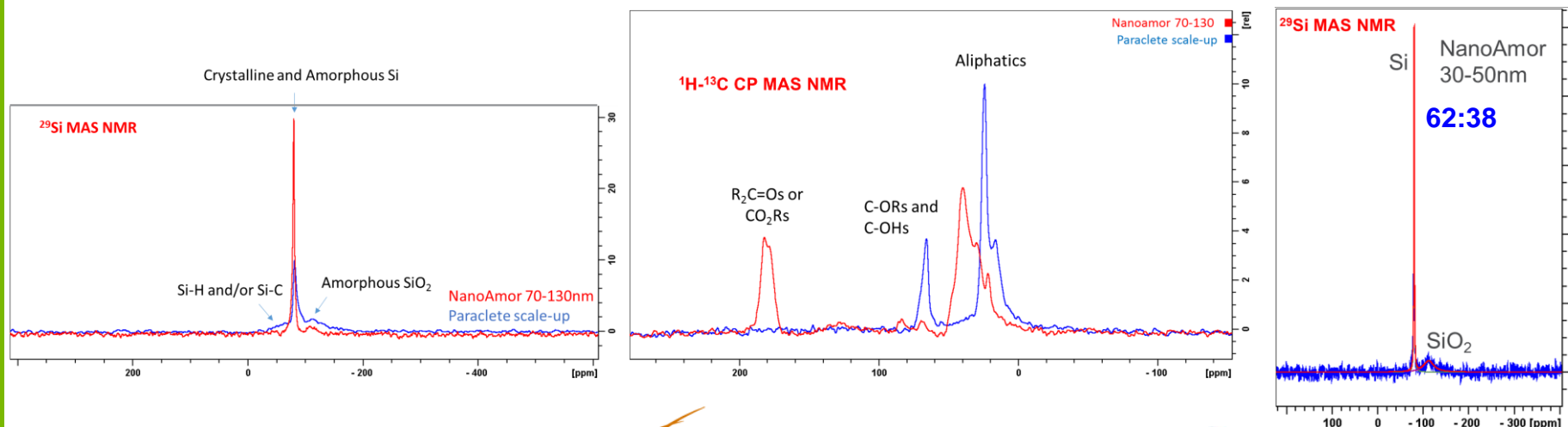


# PROBING BULK AND SURFACE CHEMISTRY OF SILICON

## Not all commercial silicon powders are created equal: HydroQuebec vs. Aldrich vs. NanoAmor vs. Paraclete

See BAT349 and 350

- Powders with smaller average particle sizes contain more amorphous  $\text{SiO}_2$  content
- Paraclete powder was found to contain a significant amorphous-Si and Si-C/H content when compared to similar particle sized NanoAmor powders.
- An organic coating detected for both Paraclete and NanoAmor powders and none for HydroQuebec powder.
  - The chemistry of the coatings are different for different manufacturers with different functional groups: Generates processing and e-chem differences



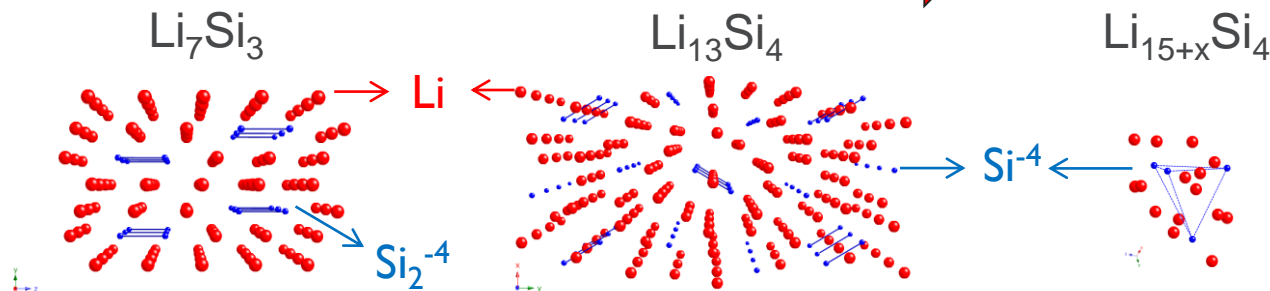


# APPROACH

- Study reactions that may cause coulombic inefficiencies and self-discharge, study the best representative model compounds of Li-Si system:

Highly charged silicon anions

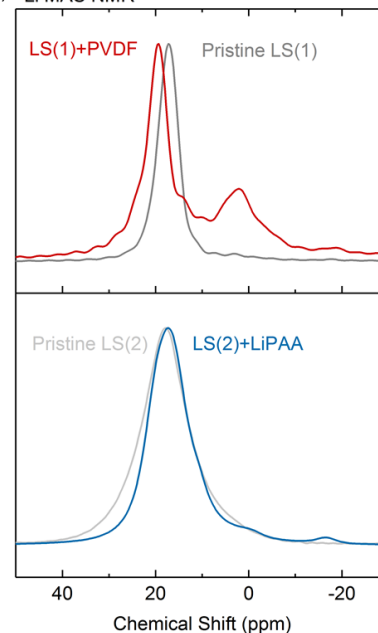
- $\text{Li}_7\text{Si}_3$
- $\text{Li}_{13}\text{Si}_4$
- $\text{Li}_{15+x}\text{Si}_4$



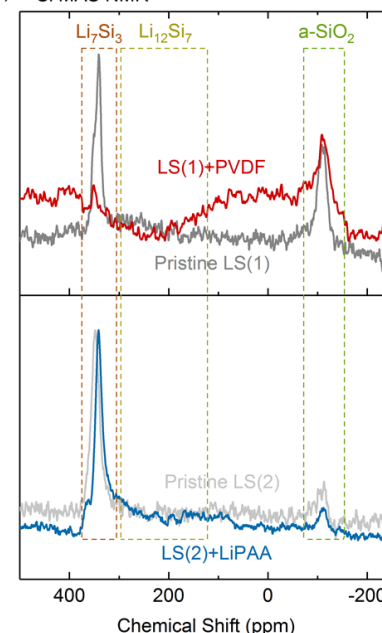
- Expose the Li-Si model compounds to:

- Binders
  - LiPAA (stable)
  - PVDF (unstable)
- Electrolyte components
  - EC
  - EMC
  - FEC
  - Glymes
  - Other solvents

(a)  $^7\text{Li}$  MAS NMR



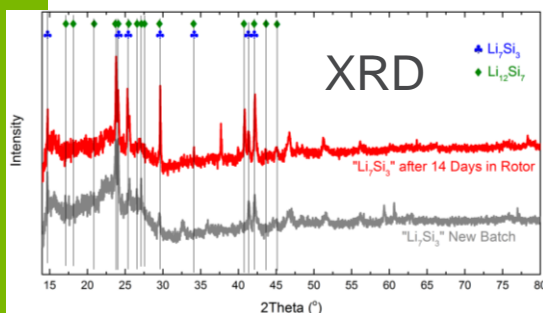
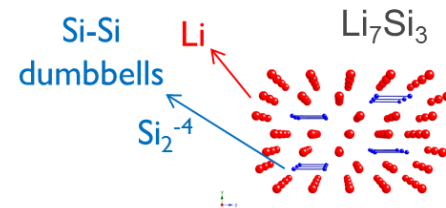
(b)  $^{29}\text{Si}$  MAS NMR



# $^7\text{Li}$ MAS NMR and XRD of $\text{Li}_7\text{Si}_3$ : Stability in zirconia rotor

Pristine  $\text{Li}_7\text{Si}_3$  reacts even with the  $\text{ZrO}_2$  high precision ceramic rotor with Li loss as a function of time.

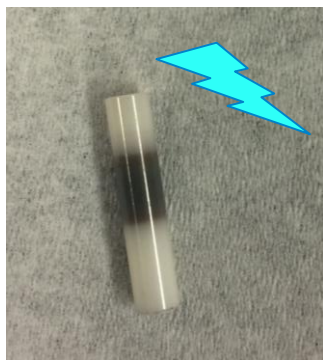
Highlights the reactivity challenges associated with freshly synthesized lithium silicides



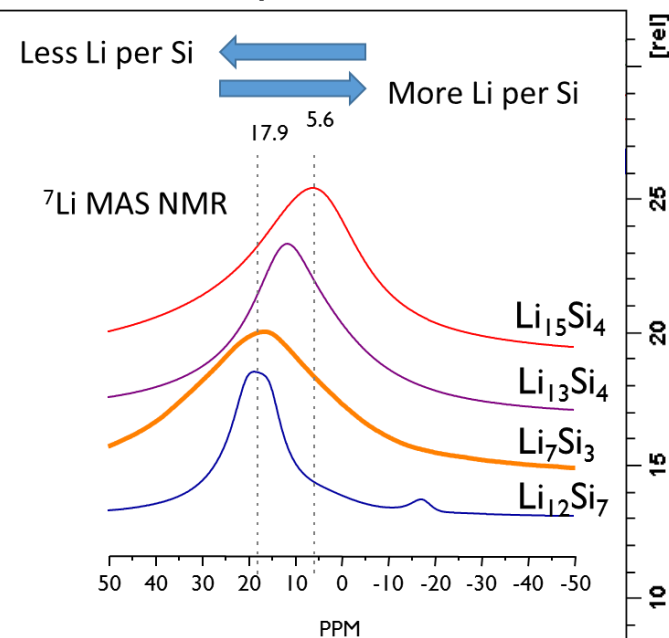
← Positive shift indicates less Li per Si

$\text{Li}_7\text{Si}_3$  (7 Days)  
Pristine  $\text{Li}_7\text{Si}_3$  (4 Day)

$\text{Li}_7\text{Si}_3$  (14 Days)



Formation of a phase with diamagnetic Li salt(s)



Key et al. JACS, 2009

# Li<sub>7</sub>Si<sub>3</sub> REACTIVITY - BINDERS

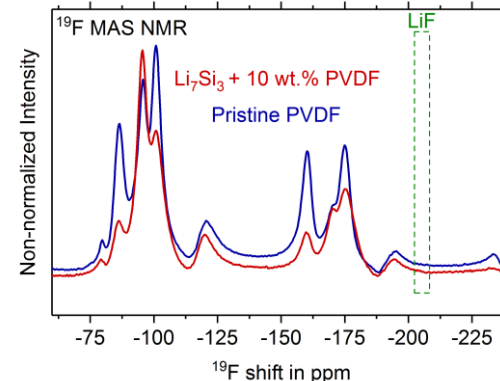
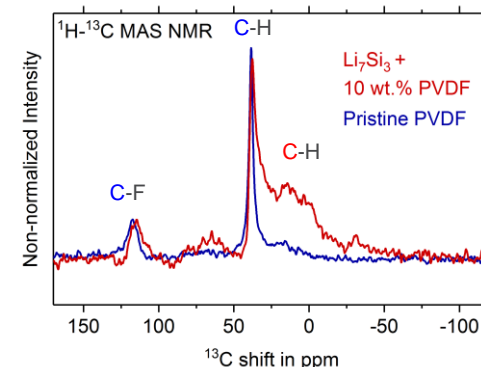
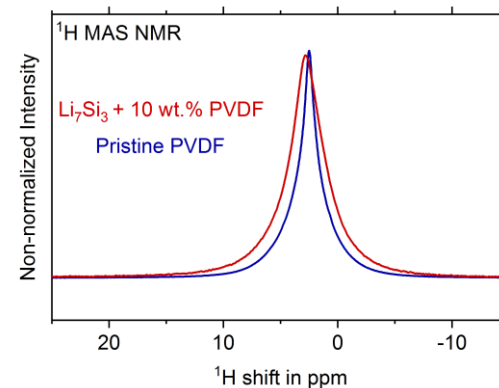
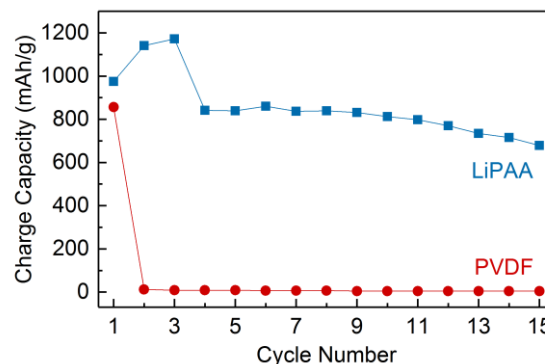
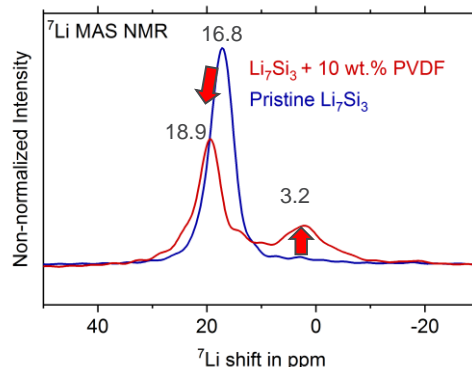
When binders are physically mixed with Li<sub>7</sub>Si<sub>3</sub> in inert conditions (Ar): PVDF binder aliphatic carbons react while no defluorination via LiF formation was observed.

- Li<sub>7</sub>Si<sub>3</sub> model compound has been shown to react;

- Extensively with PVDF

- <sup>7</sup>Li NMR suggests significant loss of Li and Formation of diamagnetic Li salts
- <sup>19</sup>F NMR detects change in binder fluorine groups while no LiF was detected
- <sup>1</sup>H and <sup>13</sup>C NMR shows formation of new aliphatic functionalities

- Minor reaction with LiPAA



# Li<sub>7</sub>Si<sub>3</sub> REACTIVITY - BINDERS

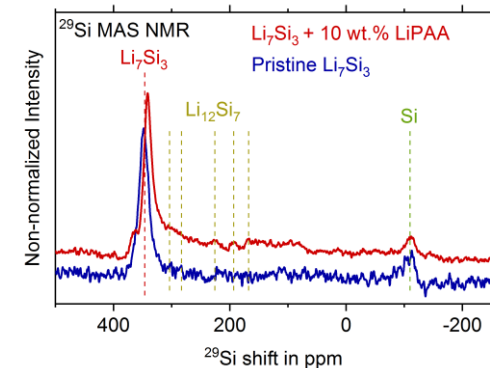
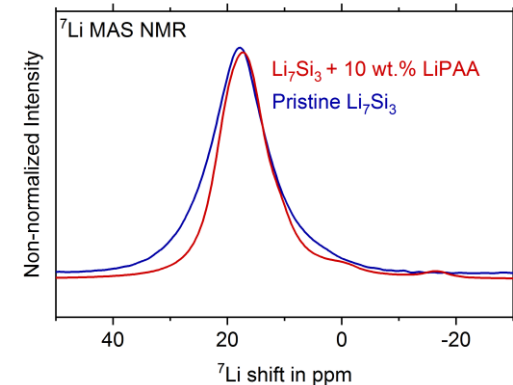
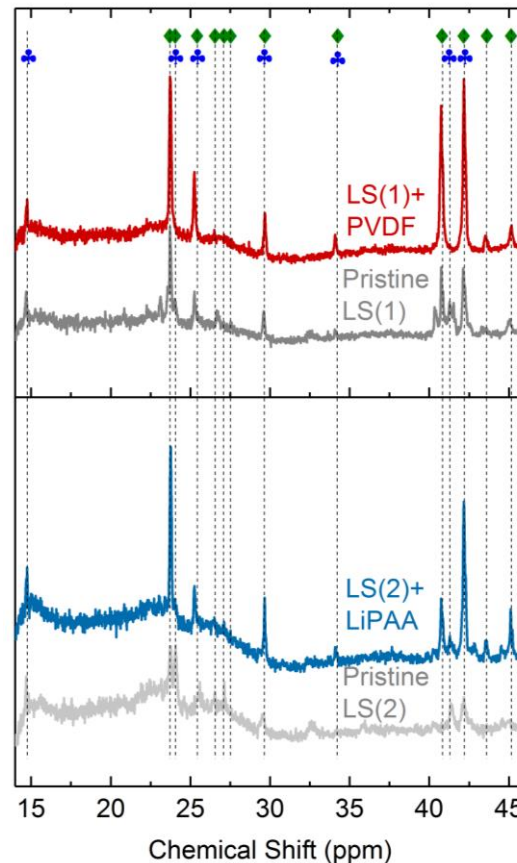
Minimal changes observed for the active material in LiPAA case.

- Li<sub>7</sub>Si<sub>3</sub> model compound has been shown to react;
  - Extensively with PVDF

- <sup>7</sup>Li NMR shows significant loss of Li and formation of diamagnetic Li salts

- Minor reaction with LiPAA

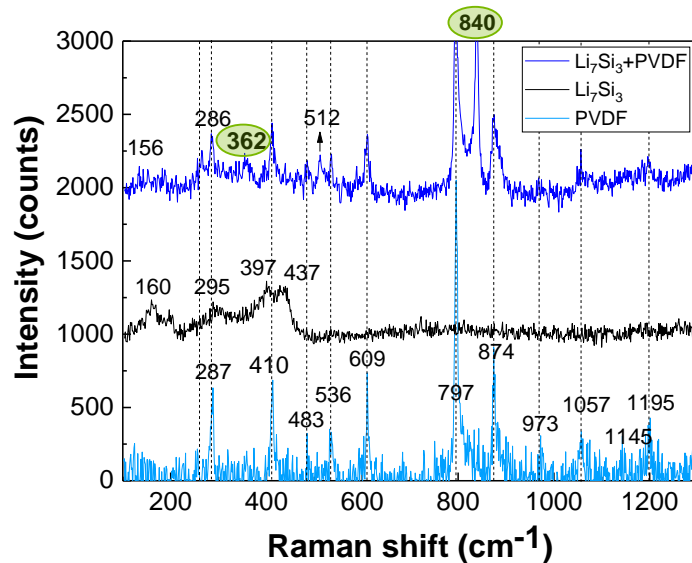
- <sup>29</sup>Si, <sup>7</sup>Li NMR and XRD shows slight Li loss and formation of Li<sub>12</sub>Si<sub>7</sub>



# RAMAN SPECTRA: THE $\text{Li}_7\text{Si}_3$ PHASE AND ITS MIXTURE WITH PVDF AND LIPAA

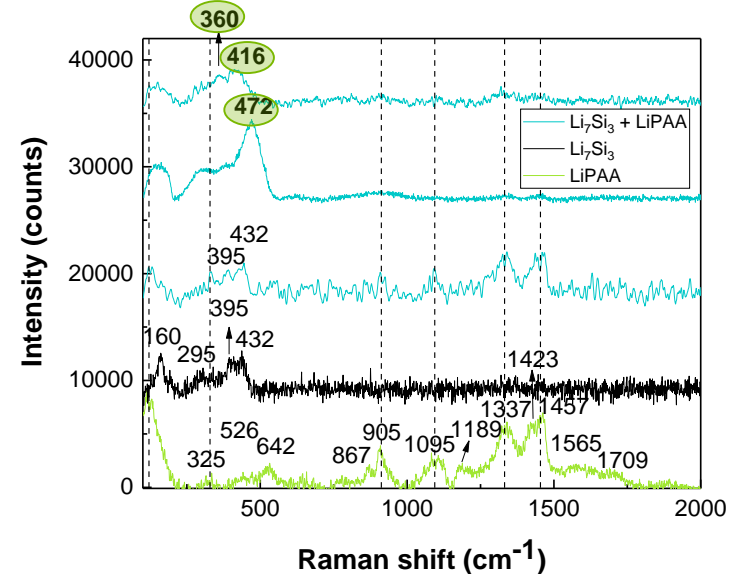
Mixtures consisting of 70 wt. %  $\text{Li}_7\text{Si}_3$  powder and 30 wt. % of binder. Delithiation and formation of Si-F bands were detected for PVDF mixture. Minor changes for LiPAA.

$\text{Li}_7\text{Si}_3$  + PVDF



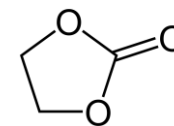
The vibrations of the “ $\text{Li}_7\text{Si}_3$ +PVDF” mixture mainly combine those observed for PVDF and Si-related species. In certain areas however the  $\text{Li}_7\text{Si}_3$  seems to evolve to the delithiated  $\text{Li}_{12}\text{Si}_7$ , as the band at  $362 \text{ cm}^{-1}$  suggests. In the mixture, the formation of Si-F compounds is also observed at  $840 \text{ cm}^{-1}$  ( $\nu_a$ , Si-F).

$\text{Li}_7\text{Si}_3$  + LiPAA



In the “ $\text{Li}_7\text{Si}_3$ +LiPAA” mixture, the vibrations of  $\text{Li}_7\text{Si}_3$  are commonly hidden by the intensity of LiPAA bands making the analysis challenging. Overall only slight changes were detected. Depending on the region: i) no band shifting is observed for  $\text{Li}_7\text{Si}_3$ ; ii)  $\text{Li}_7\text{Si}_3$  becomes amorphous (see a-Si band at ca.  $470 \text{ cm}^{-1}$ ) iii) the presence of some  $\text{Li}_{12}\text{Si}_7$  ( $360$  and  $416 \text{ cm}^{-1}$ ) was observed.

# In-situ $^7\text{Li}$ MAS NMR of $\text{Li}_7\text{Si}_3 + \text{EC}$

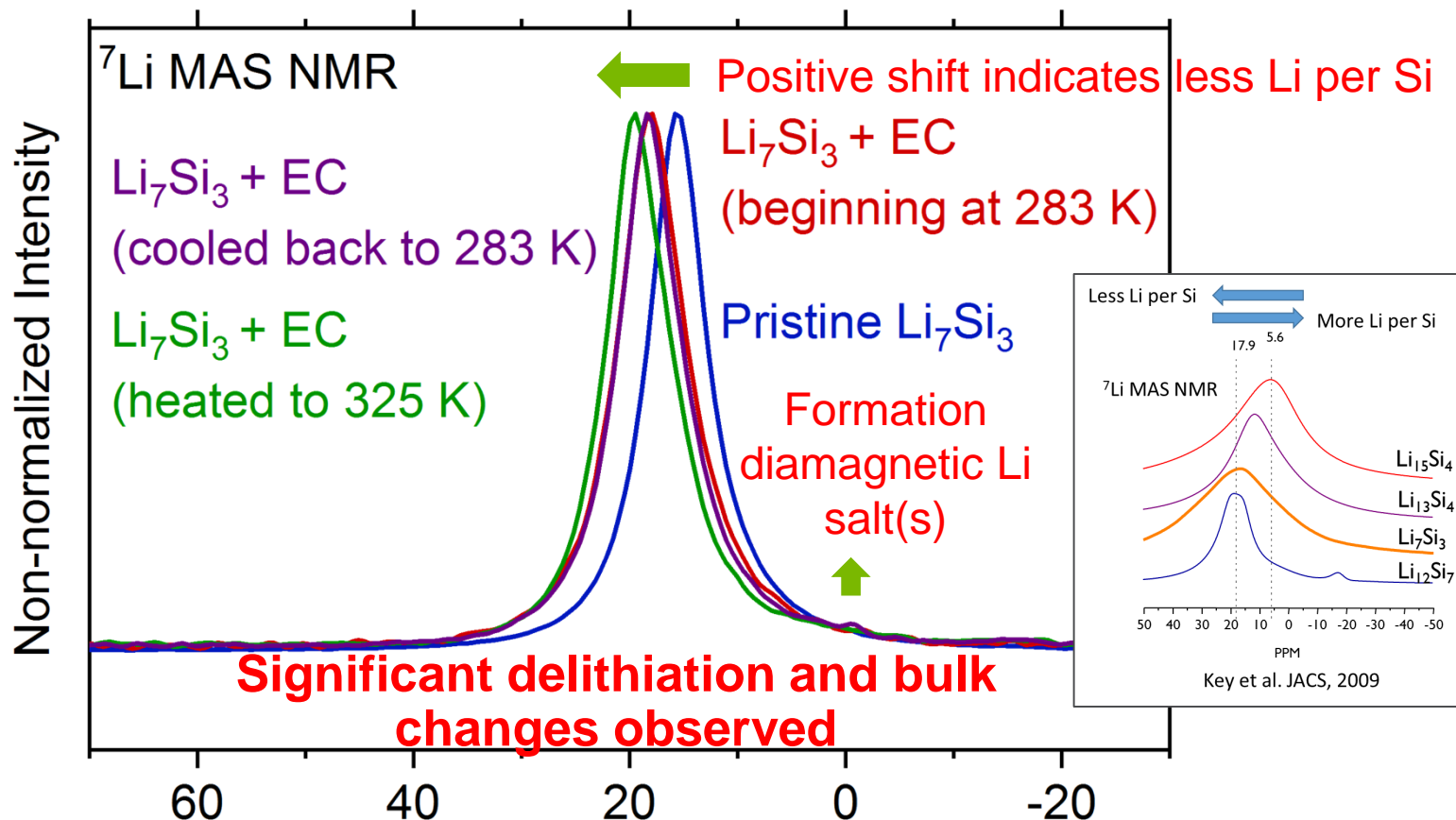


Melting point:  
307-310 K

When mixed  $\text{Li}_7\text{Si}_3$  with solid EC, the main peak shifted by +2.2 ppm

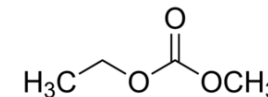
When heated up to 325 K, the main peak shifted by +3.9 ppm

When cooled back to 298 K, the main peak shifted by +2.6 ppm





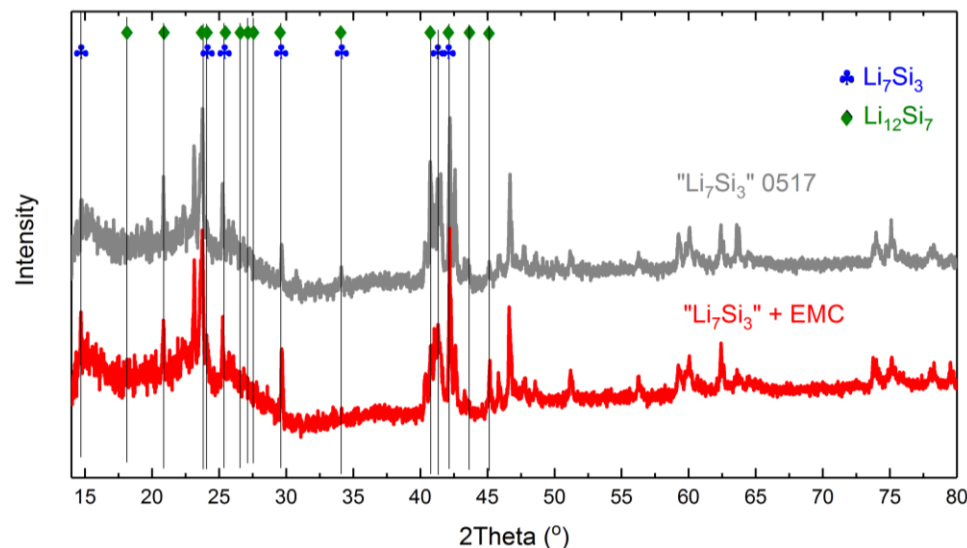
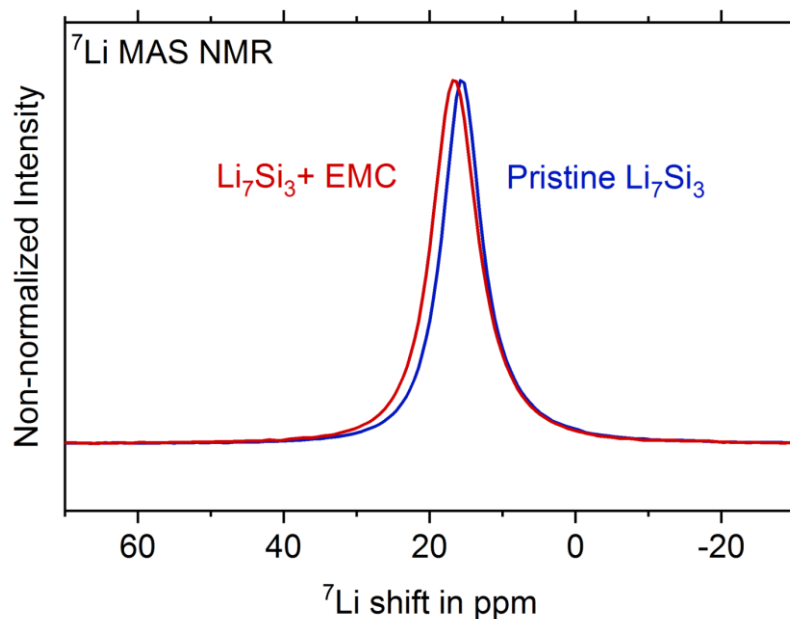
# $^7\text{Li}$ MAS NMR of $\text{Li}_7\text{Si}_3$ + EMC and XRD (post-evaporation of EMC in Ar-glovebox)



When soaked in EMC, the main peak shifted by +1.1 ppm.

Only subtle changes can be observed in XRD after mixing with EMC, increase in  $\text{Li}_{12}\text{Si}_7$

Minor delithiation and bulk changes observed



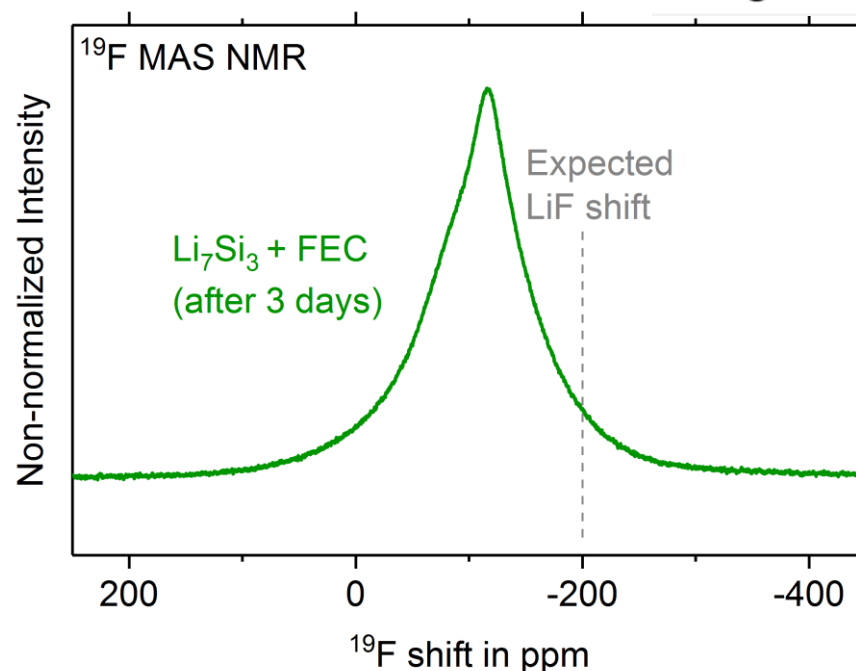
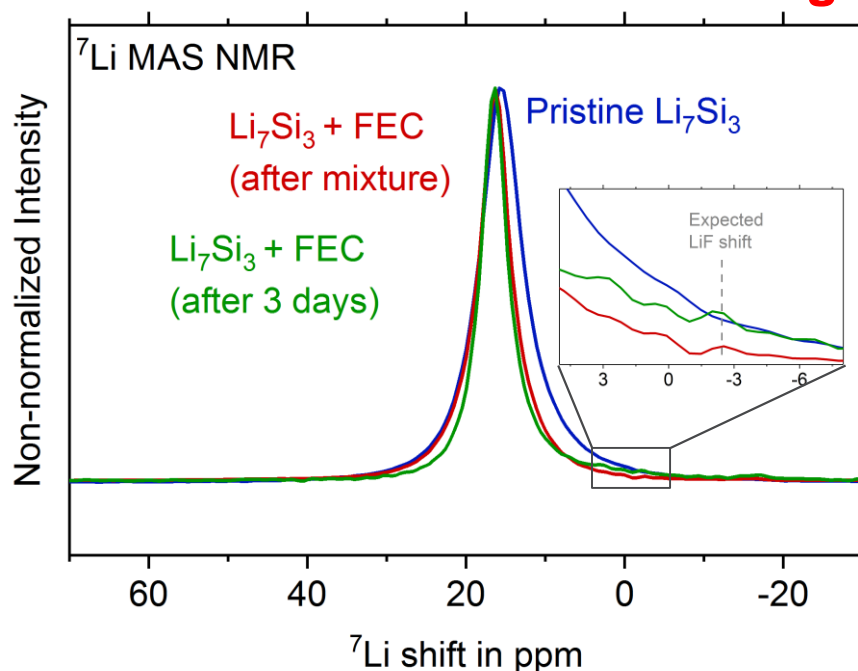
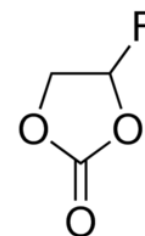


# $^7\text{Li}$ and $^{19}\text{F}$ MAS NMR of $\text{Li}_7\text{Si}_3 + \text{FEC}$

When soaked in FEC, the main peak shifted by +0.7 ppm. No  $\text{LiF}$  formation detected.

Passivation in electrochemical setting could be different...

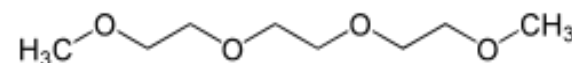
**Minor delithiation and bulk changes observed**



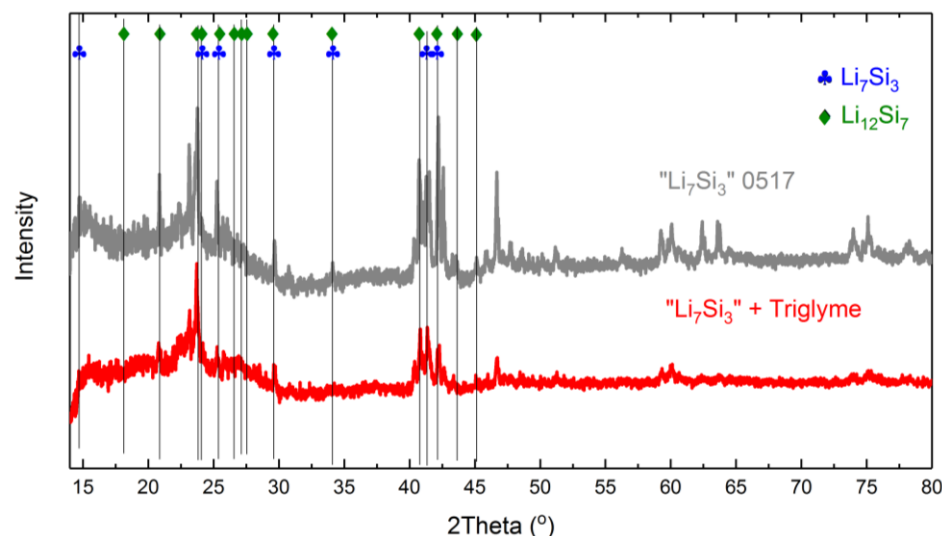
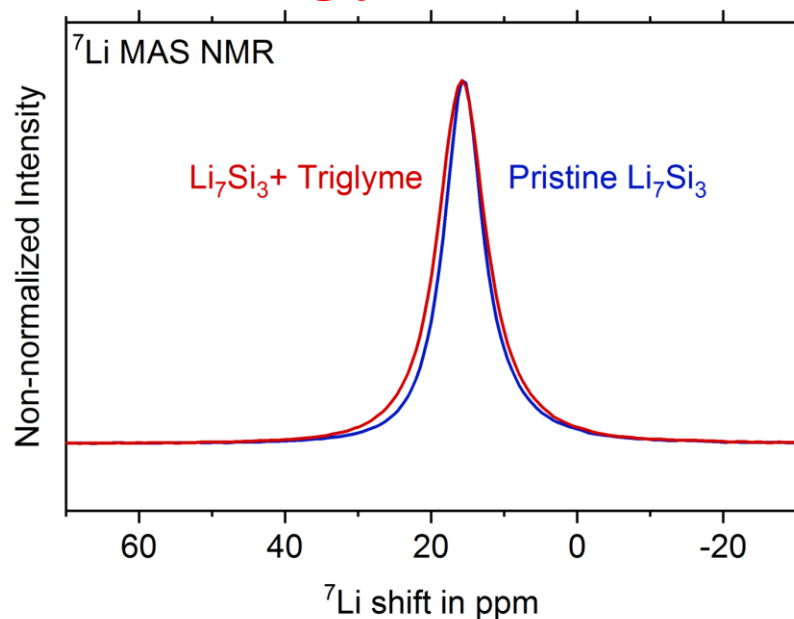
# $^7\text{Li}$ MAS NMR of $\text{Li}_7\text{Si}_3$ + Triglyme and XRD (post evaporation of Triglyme in Ar-glovebox)

When soaked in Triglyme, the main peak shifted only by +0.2 ppm.

Minimal phase changes in XRD.



No changes in bulk and Li content. Results consistent with relative inertness of glymes.

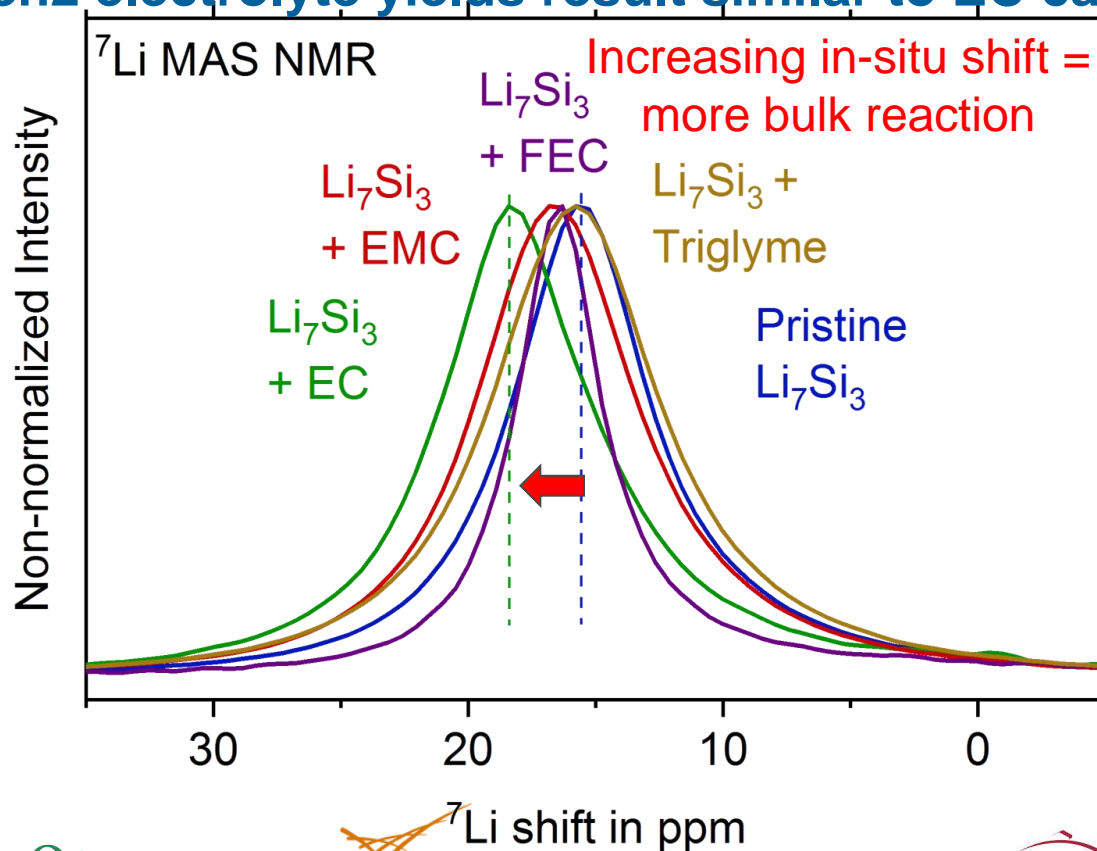


# $^7\text{Li}$ MAS NMR Comparison

$\text{Li}_7\text{Si}_3$  + Triglyme leads to the least peak shift and found to be quite inert. EMC and FEC was also remarkably inert against the model compound.

$\text{Li}_7\text{Si}_3$  + EC leads to the most peak shift.

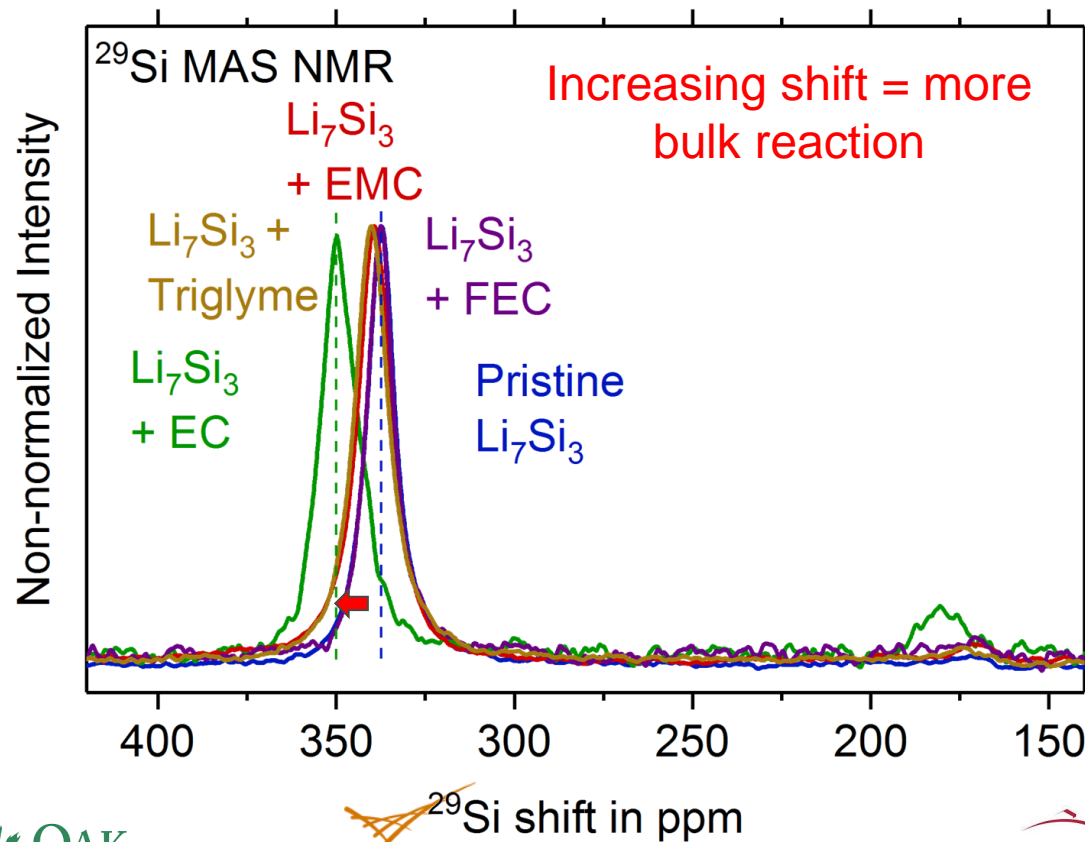
Test with Gen2 electrolyte yields result similar to EC case.



# $^{29}\text{Si}$ MAS NMR Comparison

After reaction with EC, the main peak shifted by +12.5 ppm with a new peak formed at 180 ppm.

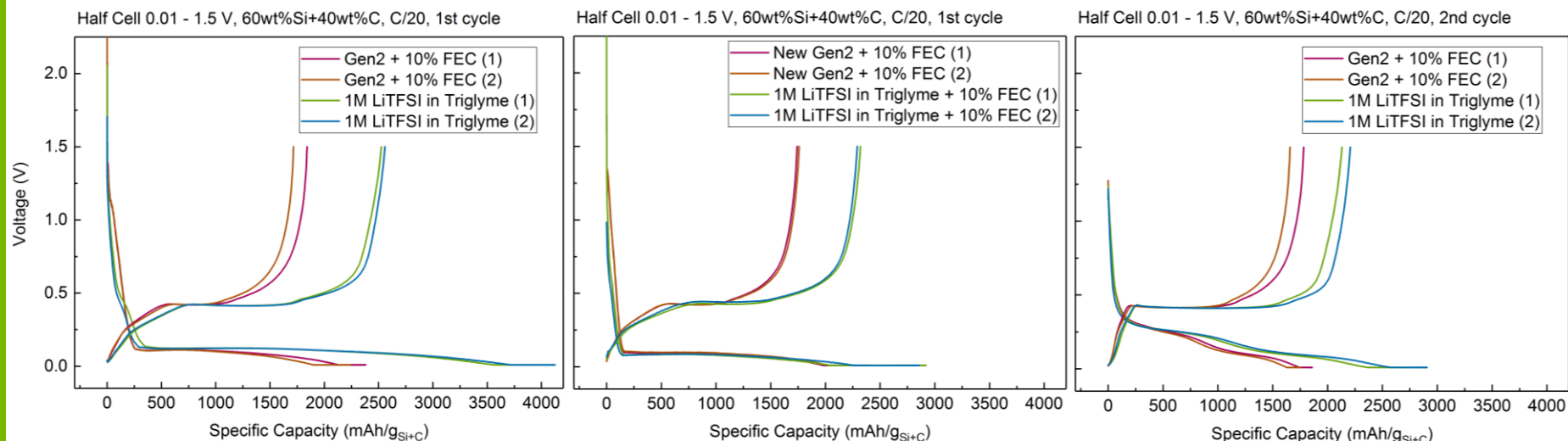
With Triglyme/EMC/FEC, the peak shifted only by +2.6/+1.9/+0.3 ppm, confirming  $^7\text{Li}$  NMR results.



# Electrochemical Test with a Triglyme based Electrolyte vs. Baseline (1<sup>st</sup> cycle)

Very few reports in literature on use of glymes for silicon: *Energy Environ. Sci.*, 2016, 9, 3262 – promising results

**Much higher initial charge/discharge capacity was observed using a triglyme based electrolyte consistent with a hypothesis of inhibited capacity loss (self-discharge)**

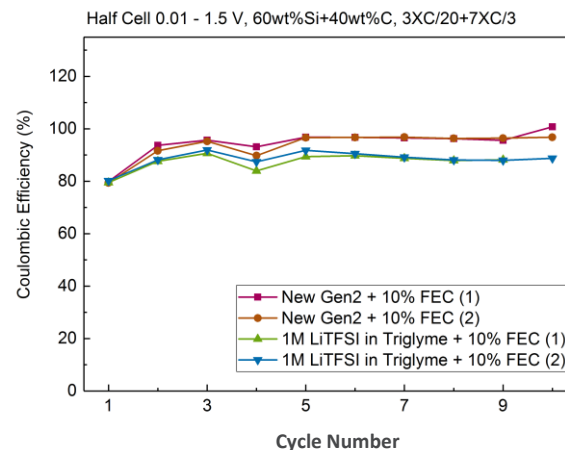
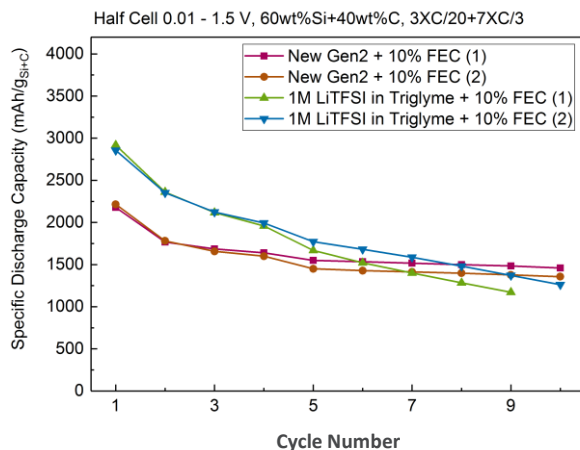
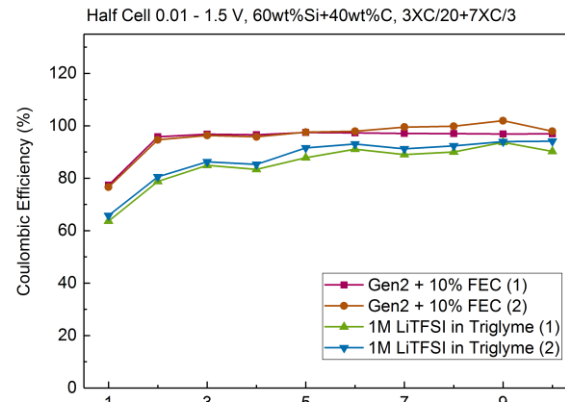
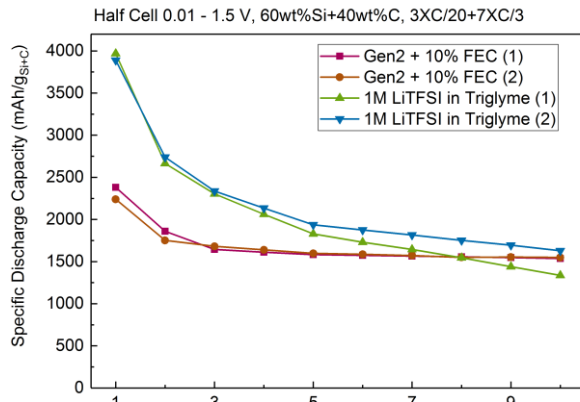


60%wt Si + 40wt% hard C drop-cast electrodes vs. Li

# Electrochemical Test with Triglyme Electrolyte

## Capacities and Efficiencies

Triglyme leads to fast capacity fading, lower coulombic efficiency and lower initial capacities with FEC. **Suggests non-passivation.**



60wt Si + 40wt% hard C drop cast powders vs. Li

# SUMMARY

- An NMR methodology was developed to quantify and study amorphous  $\text{SiO}_2$  shells and coatings in commercial silicon powders
  - Effect of heat treatments and electrode processing investigated
    - Gassing reactions and effects on silicon surfaces and terminations identified
    - Silicates on commercial powders improved performance with annealing
  - Different “coatings” and  $\text{Si}:\text{SiO}_2$  ratios characterized on commercial sources leading to differences in processing (former) and electrochemical performance (both)
- The reactivity of the  $\text{Li}_7\text{Si}_3$  with PVDF and LiPAA has been studied:
  - Minimal reaction detected for LiPAA case
  - Significant delithiation detected for PVDF case
    - $\text{Li}_{12}\text{Si}_7$  and an amorphous Li-salt formation in the bulk is accompanied with changes in C-H moieties in the binder while some Si-F band formation without any LiF formation was observed
- In-situ MAS NMR results show that  $\text{Li}_7\text{Si}_3$  model compound react the most with EC, less with FEC/EMC/triglyme. Reactions result in bulk delithiation.
- Using triglyme electrolyte leads to much higher capacity which is consistent with model reactivity work but with lower coulombic efficiency and poor capacity retention; could be indicative of non-passivating behavior
- Simply adding FEC to triglyme electrolyte does not help to improve the cyclability; highlights the need to characterize and understand the new SEI or lack thereof in a new chemistry



# FUTURE STUDY

## Short term:

- Post electrochemistry characterizations on triglyme cell Li and Si electrodes
- Full-cell tests with triglyme electrolyte
- $\text{Li}_{13}\text{Si}_4$  reactivity test with electrolyte components
  - Probe reaction with FEC and formation of LiF at lower voltage model system
- Speciation of organic decomposition products on model compounds from reactivity studies

## Long term:

- Work with electrolyte teams to explore opportunities in identifying new electrolyte formulations in both carbonate and non-carbonate chemistries guided by model compound reactivity studies
- Work with SEISta fundamental questions on silicon corrosion/side reactions (tied to model compound reactivity studies) and role and evolution of silicates and lithium silicates (tied to quantification of  $\alpha\text{-SiO}_2$ )

Any proposed future work is subject to change based on funding levels.

# RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

Last year two poster presentations covered all the project. The two posters were each reviewed by eight reviewers. We thank the reviewers for their thoughtful comments. Selected excerpts are given below.

- Many of the reviewers' comments were generally positive.
  - “applauded the excellent, thorough approach”
  - “very ambitious program to assess advantages, disadvantages and solutions for Si anode materials”
  - “very nice intra-laboratory coordination”
- One reviewer thought we could further enhance the program by bringing in experts in mechanical stresses. We conduct limited mechanical measurements and have relied on literature to establish a stable particle size, but in general we agree more in-depth studies could improve the program.
- One reviewer suggested that our commitment to openness limits our ability to examine proprietary materials. We agree totally and recognize the limitation. However, we consider that the work we are doing is addressing the fundamental issues with silicon materials and will benefit the entire community.

# REMAINING CHALLENGES AND BARRIERS

- Several key challenges remain that limit integration of silicon into graphitic negative electrodes, mostly related to the large crystallographic expansion of silicon (>300%) upon lithiation.
  - SEI stability issues, which affect cycling efficiency.
  - Electrode stability issues that include particle isolation, accommodating volume changes, and adherence.

## COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Six National Laboratories have teamed to form this integrated effort focused on gaining insights into and advancement of silicon-based materials, electrodes, and cells.
- This effort has strong interactions with the Silicon Electrolyte Interface Stabilization (SEI-Sta) project (BAT344, BAT345, BAT346, BAT347, and BAT348).
- Paraclete Energy is supplying baseline silicon materials.

# CONTRIBUTORS AND ACKNOWLEDGMENT

## Research Facilities

- Post-Test Facility (PTF)
- Materials Engineering Research Facility (MERF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Battery Manufacturing Facility (BMF)
- Battery Abuse Testing Laboratory (BATLab)

## Contributors

- |                   |                       |                            |                           |
|-------------------|-----------------------|----------------------------|---------------------------|
| ▪ Daniel Abraham  | ▪ Steve George        | ▪ Min Ling                 | ▪ Seoung-Bum Son          |
| ▪ Eric Allcorn    | ▪ Jinghua Guo         | ▪ Gao Liu                  | ▪ Caleb Stetson           |
| ▪ Seong Jin An    | ▪ Binghong Han        | ▪ Wenquan Lu               | ▪ Robert Tenent           |
| ▪ Beth Armstrong  | ▪ Atetegeb Meazah     | ▪ Maria Jose Piernas Muñoz | ▪ Lydia Terborg           |
| ▪ Chunmei Ban     | Haregewoin            | ▪ Jagjit Nanda             | ▪ Wei Tong                |
| ▪ Javier Bareno   | ▪ Kevin Hays          | ▪ Kaigi Nie                | ▪ Stephen Trask           |
| ▪ Ira Bloom       | ▪ Bin Hu              | ▪ Ganesan Nagasubramanian  | ▪ Jack Vaughey            |
| ▪ Anthony Burrell | ▪ Andrew Jansen       | ▪ Christopher Orendorff    | ▪ Gabriel Veith           |
| ▪ Peng-Fei Cao    | ▪ Gerald Jeka         | ▪ Bryant Polzin            | ▪ David Wood              |
| ▪ Yang-Tse Cheng  | ▪ Sisi Jiang          | ▪ Krzysztof Pupek          | ▪ Yimin Wu                |
| ▪ Claus Daniel    | ▪ Christopher Johnson | ▪ Marco-Tulio F. Rodrigues | ▪ Koffi Pierre Claver Yao |
| ▪ Dennis Dees     | ▪ Kaushik Kalaga      | ▪ Philip Ross              | ▪ Taeho Yoon              |
| ▪ Fulya Dogan Key | ▪ Baris Key           | ▪ Rose Ruther              | ▪ Ji-Guang Zhang          |
| ▪ Wesley Dose     | ▪ Joel Kirner         | ▪ Niya Sa                  | ▪ Liang Zhang             |
| ▪ Zhijia Du       | ▪ Robert Kostecki     | ▪ Robert Sacci             | ▪ Linghong Zhang          |
| ▪ Alison Dunlop   | ▪ Gregory Krumdick    | ▪ Tomonori Saito           | ▪ Lu Zhang                |
| ▪ Trevor Dzwiniel | ▪ Jianlin Li          | ▪ Yangping Sheng           | ▪ Zhengcheng Zhang        |
| ▪ Kyle Fenton     | ▪ Xiaolin Li          | ▪ Youngho Shin             | ▪ Tianyue Zheng           |
|                   | ▪ Chen Liao           | ▪ Ilya A. Shkrob           |                           |

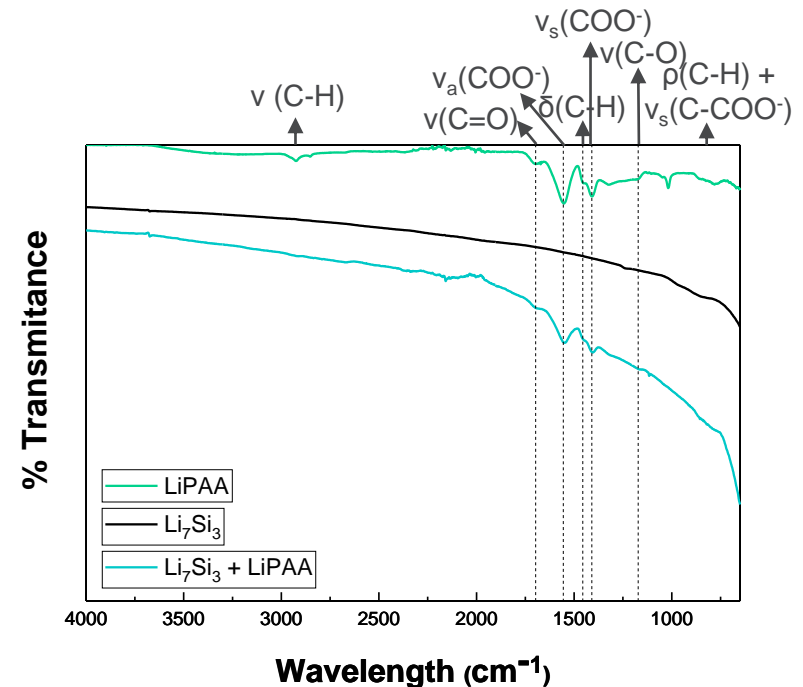
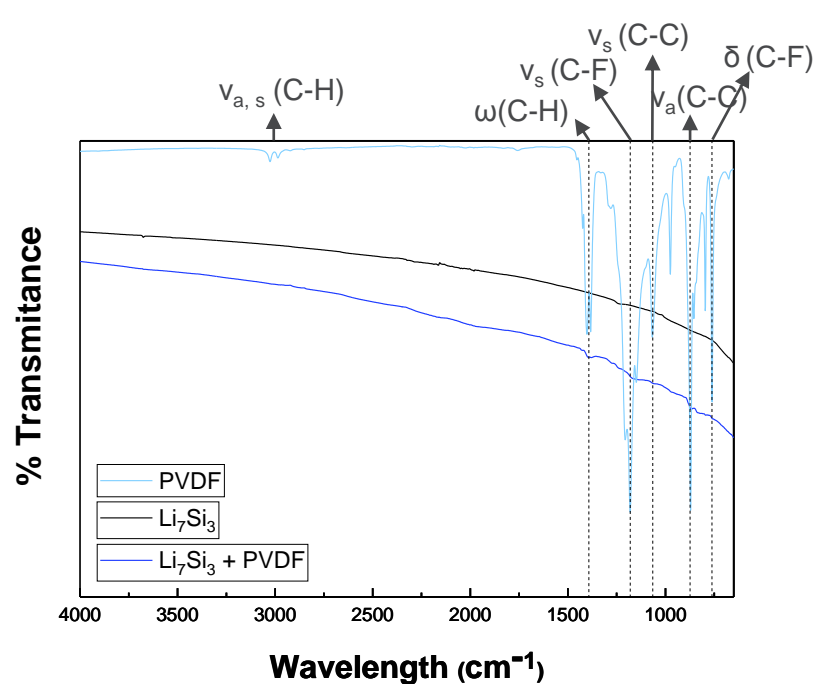
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# TECHNICAL BACKUP SLIDES

**[maximum of five]. These back-up technical slides will be available for your presentation and will be included in the web PDF files released to the public.)**

# INFRARED SPECTRA: THE $\text{Li}_7\text{Si}_3$ PHASE AND ITS REACTION WITH PVDF AND LIPAA

Mixtures consisting of 70 wt. %  $\text{Li}_7\text{Si}_3$  powder and 30 wt. % of the corresponding binder were examined



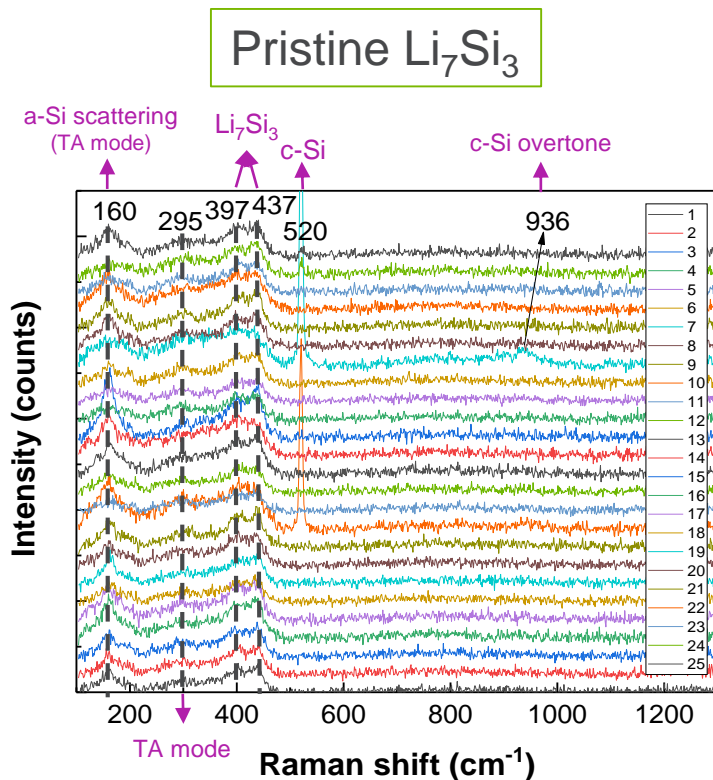
No IR activity is observed in  $\text{Li}_7\text{Si}_3$ , as expected. The  $\text{Li}_7\text{Si}_3$  + PVDF mixture solely shows the signals associated to the binder, although these are extremely attenuated and detailed analysis is challenging.

Similarly to the results with PVDF, the blend of  $\text{Li}_7\text{Si}_3$  with LiPAA basically reflects the vibrations corresponding to the binder.

# RAMAN SPECTRA: THE $\text{Li}_7\text{Si}_3$ PHASE

Measurement conditions: 10s, 5% laser power, 20 acc (for each point)

Area analyzed:  $80\text{ }\mu\text{m} \times 80\text{ }\mu\text{m}$



Almost all the spectra displayed:

- The a-Si scattering band (at  $160\text{ cm}^{-1}$ )
- The two characteristic bands of  $\text{Li}_7\text{Si}_3$  at ca.  $397$  and  $437\text{ cm}^{-1}$ .

In addition, some other vibrations associated with Si are observed (TA mode of a-Si at  $300\text{ cm}^{-1}$ ).

In some spectra, the presence of c-Si (unreacted) is also seen.